Micro X-ray Diffraction of Soil Materials: Initial Results

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Abstract No. Schu1559
Beamline(s): **X26A**

Introduction: Most of what we know about the distribution of minerals within soils is on the spatial scale of the shovel used to collect the bulk samples that are then crushed, sieved, homogenized, dispersed and size fractionated prior to x-ray diffraction (XRD) analysis. Although field observation, light microscopy, and scanning electron microscopy indicate considerable spatial variability in mineral phases over the scale of centimeters to 10s of micrometers, direct phase identification is difficult or impossible.   Even careful selective sampling usually does not provide material pure enough to identify and further characterize trace mineral phases. Our objective was to test the feasibility of using synchrotron-based microXRD to study the spatial distribution of clay-sized minerals in soils.

Methods and Materials: We prepared a number of samples in different ways to obtain experience with approaches that might be developed more fully in the future. Fungal hyphae encrusted with Mn oxides were mounted between two pieces of Prolene film. Samples of an Oxisol from Brazil, an Aquoll (containing Fe-Mn nodules) and a Udalf, both from Indiana, were impregnated with Scotchcast™ resin and self-supporting, 30 μm sections were prepared. Hand-picked Fe-Mn nodules were crushed in an agate mortar, and a few ~150 μm in diameter pieces were mounted on Kapton film. Microdiffraction was conducted on beamline X26A using a Brucker *SMART* CCD system optimized for collection of data out to higher 2 theta angles and on very weakly diffracting samples. Since X26A is optimized for spatially collimated microbeams, we have been able to obtain high-resolution microdiffraction data on very small (<10 μm) crystals.

Results: The Mn-oxide encrusted fungal hyphae contained too little material to obtain useful XRD patterns. Despite considerable scatter from the impregnating resin, kaolinite and quartz peaks were prominent in the XRD patterns obtained from the clayey soil matrix of the Oxisol. Although quartz and goethite could be identified in the microXRD patterns from thin sections of Mn nodules from the Aquoll, additional data analysis is necessary to determine whether peaks due to Mn oxide minerals are present as well. The pieces from the crushed nodules provided the best and easiest to interpret diffraction patterns, in large part because the beam traversed more than 100 μm of material, instead of only 30 μm as in the thin sections. Two pieces contained mainly goethite, with the relative diffraction line intensities close to that given in the ICDD powder diffraction database, and the simultaneously collected x-ray fluorescence (XRF) spectra indicating predominately Fe and little Mn. The third piece (Fig. 1) contained romanèchite [$Ba_{0.66}(Mn^{4+}Mn^{3+})_5O_{10} \bullet 1.34H_2O$], with XRF confirming the predominance of Mn over Fe and the presence of Ba. To our knowledge, romanèchite has never been identified in soil Mn nodules.

We have yet to determine if romanèchite can be identified from the bulk XRD pattern of nodules from this same soil.

The raw diffraction pattern of the soil material almost always consists of the diffuse rings typical of powder patterns, along with discrete, bright spots typical of diffraction from large single crystals. Additional work is necessary to determine how to best extract the powder data alone so that the relative intensities can be used for identification and peak widths can be used for crystallite size determinations.

Conclusions: Synchrotron microXRD shows great promise for providing a wealth of new information on the spatial distributions of minerals in soils and provides a tool for identifying trace mineral phases that cannot be identified using traditional bulk diffraction techniques. Developmental work is needed, however, to make the technique routine.
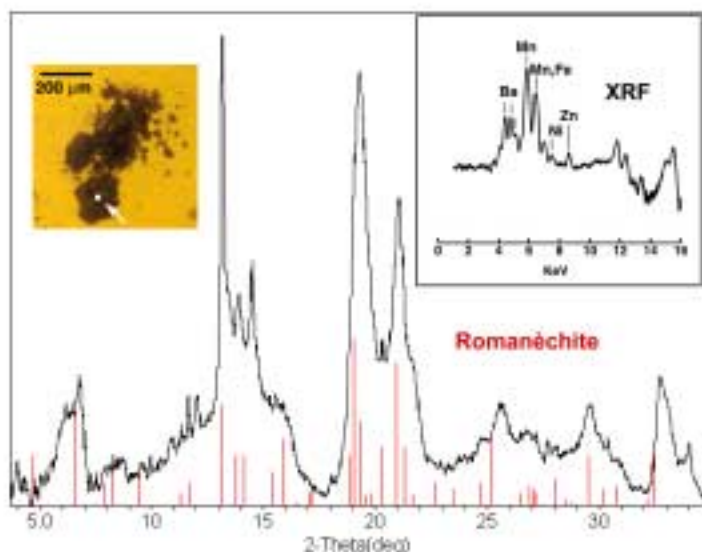
Figure 1. Diffraction pattern of romanèchite from the dark grain shown in the insert. The white spot (arrow) is the approximate size of the incident x-ray beam. The red lines are the positions of the romanèchite diffraction lines from the ICDD powder diffraction file. The XRF pattern shows that the grain contains primarily Mn and Ba.